Q2 2014

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原油高效调和先进解决方案

利用核磁共振技术的过程分析仪以最低成本支持生产调和

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魏桃树翻译

过去，炼油厂都是按照常规轻质原油的蒸馏进行设计和建设的。现在的形势是原油价格总是变化，市场对馏分油的需求也不稳定，迫使炼油厂得想方设法降低蒸馏原料的成本。降低成本的通常做法是把价格贵的轻质原油和价格便宜的劣质重油调和，或者从原油市场上购买现成的调和原油。低品质原油有已知特定产地的重油，也有贸易商从全球各地带到市场上的机会原油。这些原油由于品质差，销售价格也比较低。将这些原油与价格贵的轻质原油调和，必然会得到最优特性、最低成本、而且满足加工工艺要求的调和原油。

从工程建设和材料的角度看，全球所有的炼油厂的蒸馏都有明确定义的原油类型。这些炼油厂建造时，都是基于他们附近可用的原油类别、在市场上这类原油的成本、以及主要轻质馏分汽油的需求量。

原油蒸馏的主要目标是生产汽油馏分，例如，轻质馏分和中间馏分。最近，尤其是在美国的欧洲地区，燃料的需求从汽油转向了柴油，这就意味着过去主要是轻质原油蒸馏的炼油厂，现在必须有能力蒸馏重质原油，以提高中间馏分和重质馏分的比重。许多炼油厂还不能适应不断变化的形势，炼油毛利下降。技术限制导致许多炼油厂只能采购价格昂贵的轻质原油，但这些原油又不能特别地生产出市场上最需要的馏分。对很多炼油厂来说，这个损失特别大。很多炼油厂要么选择倒闭，要么改变他们的行为，使用调和原油进行蒸馏。

高TAN原油附加加工成本为每桶1.15-10.73美元以内，但是得到的利润每桶43.54-62.7美元

现在，原油调和要么通过调和商，要么炼油厂自己采购各种类型的低成本原油进行调和。通过调和，对低成本原油的物理、化学性质升级，以最低的成本得到一种合成原油。这种合成原油即能够在炼油厂现有的设备上加工，又能够对高附加值的馏分取得较高的收率。

原油的特征

每种原油的质量特性决定它在市场上的价值。最重要的质量特征是原油的密度，总酸值（TAN）和硫含量。API值从轻油（高API，密度小）到重油(低API,密度大)，硫以硫化氢或者多硫化合物的形式存在于原油中。这些含硫分子在蒸馏的过程中，会部分分解，形成硫化氢。原油中硫和其它酸性成分，如环烷酸，具有很强的腐蚀性。它们含量也决定原油是否为一种含酸或含硫原油。这些特征主要会导致为不同类型的原油支付不同的价格。

炼油设备

高TAN原油的特征是轻组分少、密度大、粘稠、凝固点低、氮含量大、胶质沥青质含量高、盐含量高、重金属含量高、轻质馏分收率

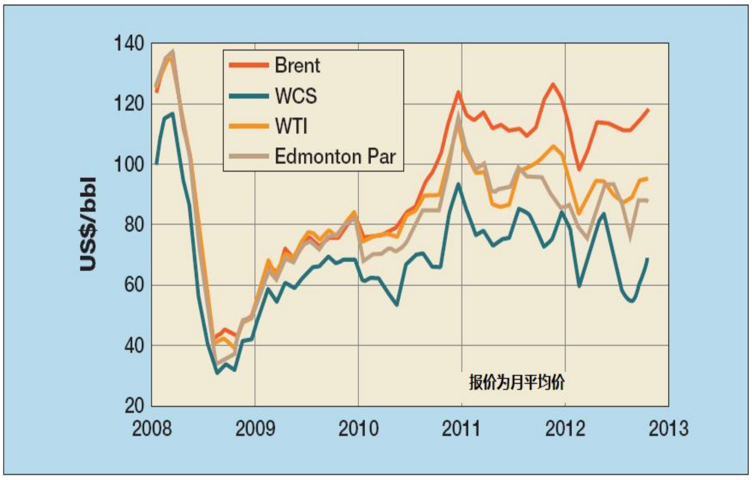

图1 根据基准世界油价

低。在脱盐装置中油的分离比常规原油更困难。这些特性也导致了这些原油的产品质量差，腐蚀性强。通常情况下，高TAN的原油被称为“机会原油”。“机会原油”的价格约为常规原油的80%。与传统原油加工相比，加工“机会原油”附加的成本为每桶$1.15-10.73，但是得到的利润为每桶$43.54-62.7。因此，使用任何可能的方式利用机会原油对炼油厂变得非常有吸引力。

在过去，大多数炼油厂都是根据可提供的和容易采购到的原油原料进行设计和建造的，这限制了很多炼油厂的适应能力，他们不能够采购不同品质的其它原油。很多的炼油厂都是按加工轻质低硫的原油进行建造，这些炼油厂加工重油就受到限制。

和轻油比，关键物理化学性质的差异，使用重油变得更加不易于提炼。重油是含酸原油，比轻油的腐蚀性强很多。重油的高粘度、强结垢趋势和不同流速让维持稳定的原油进料速率变得更难，而稳定的产品收率、产品质量的产品的可靠性需要稳定的原油进料速率。轻油和重油沸点的差异会有不同的工艺温度要求，例如预热、不同的蒸馏温度、企业的日常管理费用等。重质燃料富含有沥青质、金属和其它污染物，它们会使脱盐的效果变得很差。

产品切换

市场对某一产品的需求以及炼油厂提炼的产品都是经常变化的。据预计，2015年全球对每桶油的需求，中间馏分大约占到45%，与2005年相比，提高了10%。可以预见的是，从2009年到2030年，发展中国家的柴油、汽油生产将增加到1000万桶/天。

美国是最大的原油消费国。尽管美国的需求稳定，但中国今天排在了第二位，每年的原油消费需求增长年均4%。现在，建造新炼油厂时，已经设计成不限制于加工小范围的原油。

炼油厂的产要生产成本就是原油的价格，据估计占到现金流的80%到90%。降低原油原料的生产成本，不改变高附加值馏分的分布范围和总量，就可以提高炼油毛利。炼油厂实施采购低成本的原油，生产较高市场价值馏分的策略，直接结果就是得到炼油的利润。为提高炼油毛利，保持竞争能力，炼油厂必须使原油原料的成本最小化，而不影响生产高附加值馏分的产能。由于重油很难加工，加上与汽油相比，柴油消费比重在增加，轻质低硫的原油的市场价格又比重油高。因此，降低原油成本，不改变高附加值馏分的分布范围和总量，就提高了炼油毛利。

潜在的调和点

两类型的组织经营原油调和的业务，它们是炼油厂，或者原油调和生产贸易公司。炼油厂直接实施原油调和可得到低成本的、兼容的调和原油，用于内部消费，或者在原油贸易市场上销售。有效的原油调和为调和

商、油品贸易公司和终端提供的新的机会，它们为市场提供低成本的调和原油。这些调和原油可以保持很好的品质，高价卖给炼油厂。

原油调和可以在原油的整个供应链上实施，从井区、运输，直到炼油厂的终端调和。最终提供给蒸馏装置的原油可能是这一系列行为的总和。

原油调和策略有几个变量，每个变量对进入蒸馏装置原油最终的总体成本，以及炼油的毛利都有贡献。

炼油厂原油蒸馏装置的工程限制，炼油设备不能任何原油都能加工

不同产地、不同物性原油的成本差异，对非常规原油加工能力的提高，能够提高炼油毛利

市场上从汽油到柴油产品的变化。欧洲市场上柴油燃料需求的增加导致炼油厂增加柴油产量，超过石脑油的产量。

高粘度原油，特别是重油，在运输过程中影响原油的流动性。这些原油需要与轻质原油或者稀释剂的调和，降低粘度，提高流动性。

原油经济性

以前，炼油厂加工的原油都是来自于同一个产地。现在，炼油的利润取决炼油厂的调和能力，把少量的高成本原油与大量的低成本非常规原油调和，非常规原油有重油，超重油，高硫原油以及从油砂中提取的沥青质。当然，调和原油在保持尽可能低的成本条件下，它的特性仍然能够蒸馏装置连续稳定的生产。

基本上，原油可以分为四类：

a. 轻质低硫原油(API 30-40°, S ≤ 0.5% 质量百分比);

b. 轻质含硫原油 (API 30-40°, S=0.5-1.5%质量百分比);

c. 重质高硫原油 (API 1-30°, S =1.5 - 3.1%质量百分比);

d. 超重高硫原油 (API = 15°, S ≥ 3%质量百分比);

调和原油中某种组分的含量实际上受最大限度的生产高附加值馏分产品的物性限制，也由调和加工设备的结构限制。

以布伦特轻质原油与有点重的WTI原油当前价为基准，每桶原油的价格差异大约10美元，见图1。

“机会原油”当然会更便宜。各种原油，如委内瑞拉和加拿大的一些原油非常重，对沥青生产非常有吸引力。这些原油的加工受它们低API比重的限制。从这些原油中生产其它的馏分，必须用轻质原油或者煤油稀释。

这些重油中很多原油的另一个缺陷是高粘度。使用轻质原油、煤油或者别的稀释剂对这些原油调和也需要给他们很好的流动性，在不加热条件下能够通过管道运输。

每个炼油厂的目标就是最大限度的消费机会原油。

重油含氢低，致污物质含量高，如硫、氮、有机酸、钒、镍、二氧化硅和沥青质。低成本升级重油的方法就是使用富氢、高品质轻质原油，或者使用富氢稀释剂稀释重油，提高H/C比。

调和工艺

原油可以通过两种技术进行调和

罐内调和（批次调和）

分开存储的不同类型原油，各自以特定的体积装载到调和罐中进行调和，直到得到均一组成的调和原油。调和罐内是机械搅拌，必须取样分析以确定样品是否均一，是否满足预先设定的技术指标。如果存在差异，就必须对调和进行修正。罐内

调和的整个过程非常耗时，而且价格昂贵。

在线调和

与罐内调和相比，在线调和的完成是通过一个在线的静态混合器同时传输不同类型的原油去最终的调和罐。不同类型的原油之间预先设定的流量比，将提供的调和原油所要求的质量。通过改变不同原料的流动比，在线调和能够在线修正调和原油的品质。调和是瞬时完成的，不需要搅拌的调和罐。

为有效的操作调和工艺，没有误差，就必须要有在线过程分析仪器。它可以对调和下游进行瞬态检测，为调和操作者提供调和产品所需要的质量信息。这样，在调和过程中就能够实时在线的进行修正，保证调和原油满足预先设定的特性要求。这降低了罐内修正需要的整个罐的重新调和，以及避免不必要的质量盈余。

调和配方的确定

仿真软件，如线性规划（LP）模型，被广泛用于预测单个组分之间的比率，以制备调和产品。基于所用原油的组成数据，加上使用适当的算法，该软件通常用于计算和预测调和产品的物性。

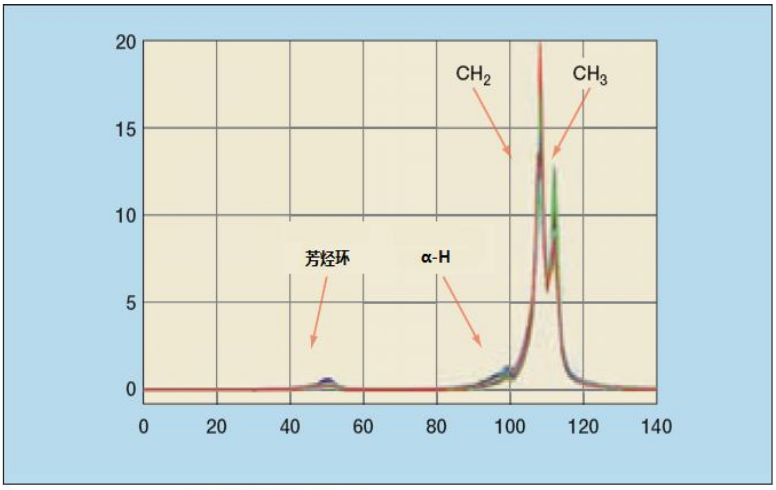

图2　典型的原油NMR谱图

软件将计算不同原油的比例，得到合适特性的调和原油，以保证所需要的馏分在最佳的收率。需要结合涵盖范围广泛的大型原油数据库，才能精确预测预先设定物性的调和原油，并有潜力最大限度的生产高附加值馏分的产品。充分调和的仿真模型不仅包括蒸馏原油的化学特性，也包括它的经济性。

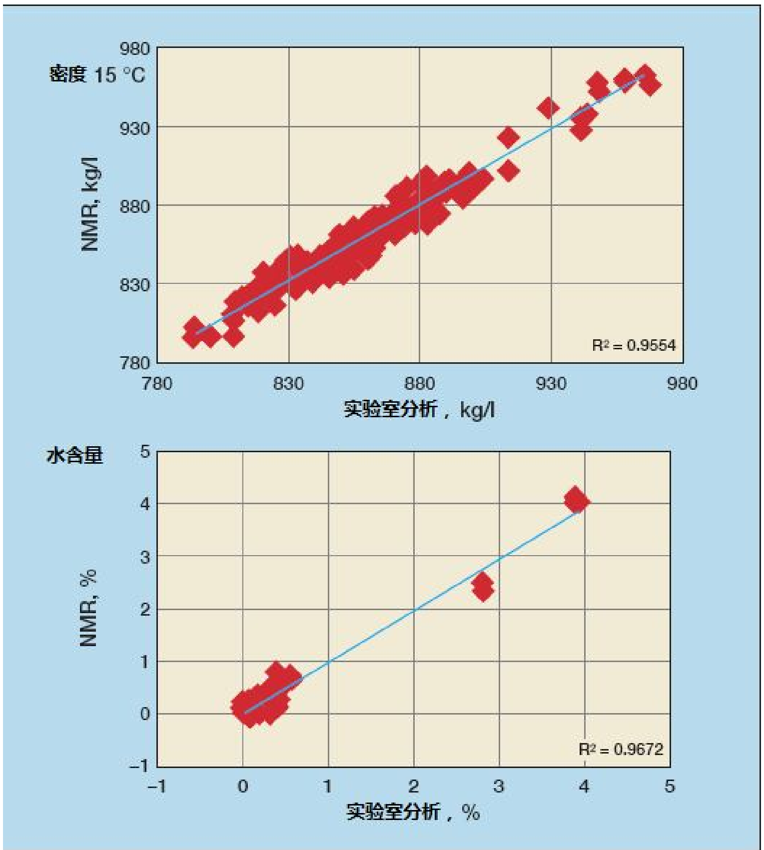

图3　NMR预测和实验室检测之间的相关性

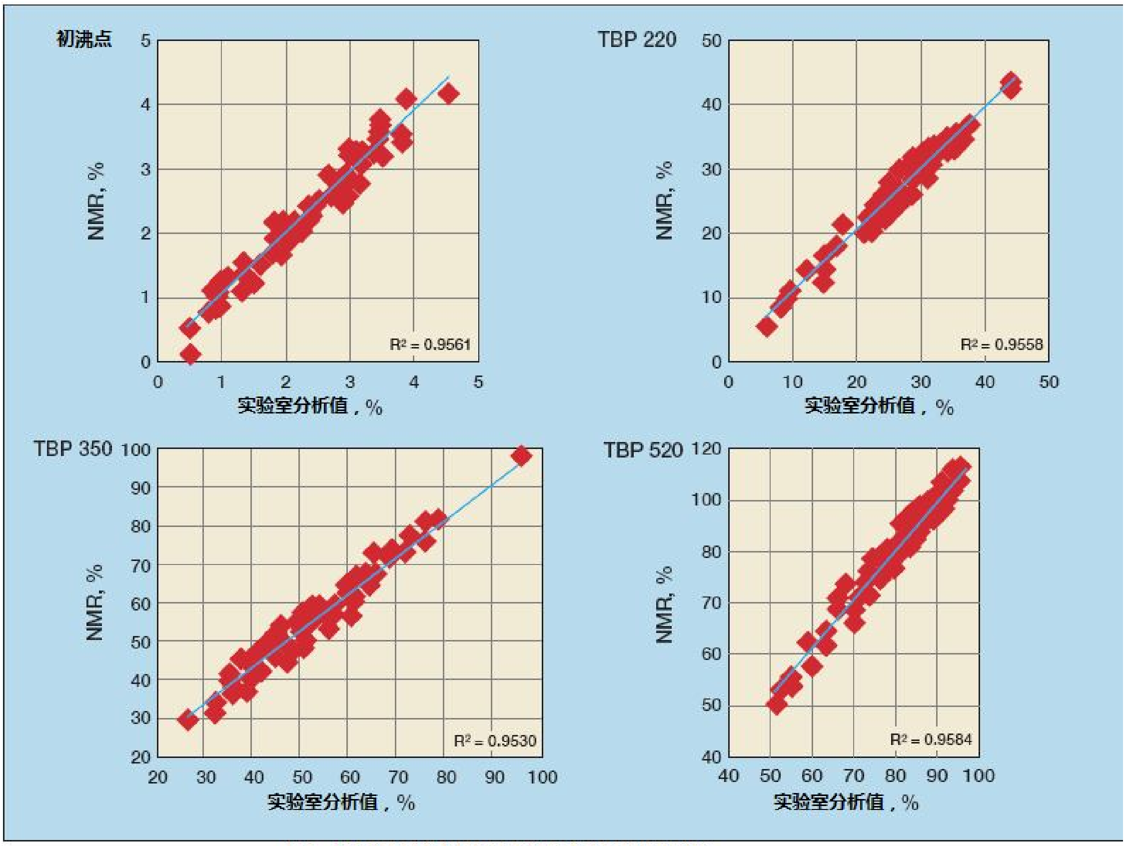

图4　NMR预测沸点与实验室测量沸点之间的相关性

它必须有能力计算出不同原油的组合，以最低的成本，提供最经济的调和原油。这样的调和原油中，成本最低的原油所占比重最大，但仍然有着最有吸引力的提炼特性。这一战略将最小化可变成本，最大化利润。

LP 建立在参与调和的不同类型原油化验数据基础之上，化验数据的任何变化，都会影响到 LP 预测的调和原油。

从根本上讲，有效的原油调和仿真软件应包括以下特征：

- 调和组分油和它们比例的计算
- 比例限制
- 预测馏分温度
- 调和原油属性约束
- 馏分属性
- 限制约束

除调和原油的物性之外，软件还应该关注到调和原油中产生的潜在利润，这就要求软件还需要涉及到：

- 各种原油的成本，以及调和原油的成本
- 最终馏分和炼油厂其它产品的价格
- 最终馏分的市场需求量

耗时和价格昂贵的实验室分析还得要，以验证调和原油的“真实”物性。如果物性没有满足，还得进行再调和。

高效原油调和需要在线监测整个生产线上调和原油的物性。不同原油的化学组成是不同的，原油不管为“纯”原油，还是调和原油，都必须持续不断的进行在线修正，以保证稳定的产品质量。这就需要对整个生产工艺调和原油的有效物性实时收集。在市场上的所有分析仪器之间，核磁共振（NMR）过程分析仪器是实现这个目标最合适的仪器。

第一台核磁共振过程分析仪器于 20 世纪 90 年代推

出，在一个特定的频率，氢核吸收和释放电磁能量。核磁共振过程分析仪的基本原理是原子核先在磁场中排列取向，然后在外部施加射频（RF）脉冲被，施加的脉冲会扭曲磁场中原子核的取向排列。共振的频率主要取决于磁场的强度。当射频脉冲结束时，质子驰豫并返回它的初始平衡位置，这个过程会产生一个衰减信号，即自由振荡衰减信号（FID）。

原油主要是碳和氢基分子有机化合物的混合物。氢原子邻近的原子，例如碳，氧和硫，以及相邻的化学键，影响磁场中氢原子核能量吸收和发射的强度。对应地，每个氢原子核在 NMR 谱上信号位移是不一致的。这些明确定义的化学位移代表不同分子的化学结构。NMR 信号的强度与氢原子的浓度线性相关，这样就能定量分析不同的氢原子核。

原油和馏分油的物性与它们的化学组成是相关的。这就可以使用化学计量学的方法，对测量的波谱数据与与原油或者其它馏分油的理化性质进行关联。与其它基于化学计量学的谱测量技术相比，如拉曼和 NIR 谱测量技术，它们是基于分子的指纹特征。由于能区分分子的特异性，以及其线性定量相

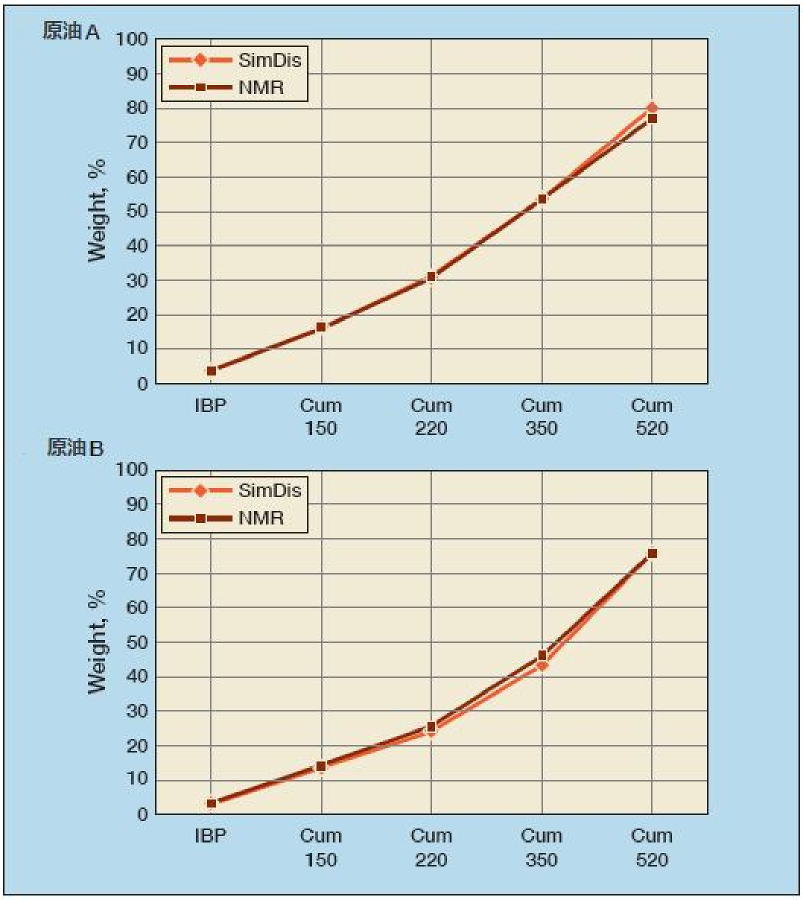

图5 重叠的NMR数据和模拟蒸馏曲线

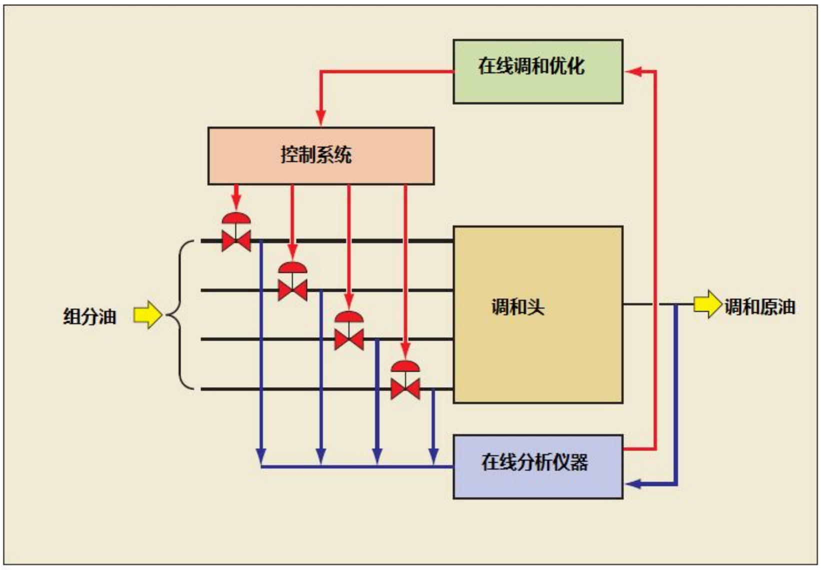

图6 整合NMR过程分析仪器，仿真模拟模型和调和控制建立原油调和站（组分油可以是高品质原油，低品质原油，稀释剂和天然气凝析液）

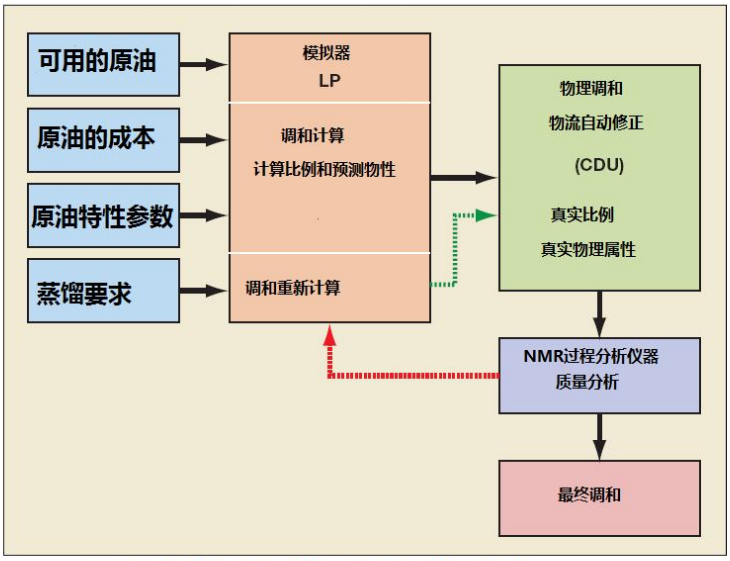

图7　动态混合过程，连续调和分析，仿真模型调整和过程控制

关的特点，NMR 技术建立化学计量学模型所需要的样本少得多。

基于 NMR 技术的在线谱仪不限于只分析透明流体，它分析透明的介质和分析不透明的介质都获得了一致好评。原油中含有水和杂原子分子，NMR 谱仪能够很好地把它们区分开来。

NMR 在线谱仪结合合适的化学计量学，能测量原油的以下属性：

- 密度
- 实沸点收率
- 芳烃含量，%
- 水含量，%
- 倾点
- 硫含量，%
- 酸值.

这些属性在原油调和中非常重要。它们的在线检测使调和得到的合成原油可以达到预定的属性，无论从理化性质的角度还是从经济的角度来看。

在线监测调和工艺避免调和产品达不到炼油厂的要求，调和错误和质量盈余也可以避免，每年节省的费用可以达到数以百万计美元。

NMR 在线分析的准确度

新一代 NMR 在线过程分析仪器的特点是 NMR 过程谱仪的分析结果与实验室检测结果之间关联精度极高。NMR 磁体对温度变化极其敏感，由于电子部件和导热检测探头产生热量的聚焦，早期的 NMR 在线过程分析仪器对温度差异尤其敏感。新一代的核磁共振过程分析仪，整体设计中排除了任何热量在磁铁或其温度不可控的周围的累积。提高了仪器的稳定性，允许温度波动从±2℃提高到±10℃。这意味着原油调和之前、或者脱盐之后所需要的任何加热，只要在±10℃的温度偏差被维持，就能够不影响分析结果。

图 3 到图 5 显示不同原油的 NMR 预测分析结果与实验室分析结果的相关性。

这些数据显示了 NMR 预测分析结果与实验室检测结果高度精确相关。这些检测分析部分是化学量，如水含量，硫含量。部分是物理量，如蒸馏曲线，以及模拟蒸馏结果与 NMR 分析结果吻合极好。考虑到实验室原油分析所需要的时间，原油化验所需要的成本，或者仪器的采购与维护成本，证明原油调和工艺中使用核磁共振过程分析仪器，特别是原油在线调和工艺，NMR 能够准确跟踪调和原油的质量，并且在必要的情况下，改变不同原油间的调和比例，以保证和维持成品调和原油的质量。

原油调和站的优化

原油调和站有调和撬，用于接收流体或者气体介质，优化软件和分析设备。分析设备应该能够在线检测操作操作中组分和产品流的数据。这些数据会传送给优化软件，调和软件的目标就是保持调和原油产品的成本最小，质量盈余最低，个体

原料属性偏差最小。为了达到这个目标，优化系统使用在线分析仪器持续接收最终产品的品质反馈。

使用在线分析仪器提供的输入，基于调和头获得的产品样品的质量信息，优化系统即可以进行原料前馈控制，也可以进行原料反馈控制。

无论LP模拟还是NMR过程分析，都可以单独实施。然而，实现原油调和工艺的最佳优化，就必须将两种技术结合起来。

高效调和优化是一个动态过程，涉及到混合，连续调和分析，仿真模型调整和过程控制。这些要素都必须考虑到，见图7。这个操作链上任何环节的缺失都会影响到整个流程的效率，并且会降低收入。

在线 NMR 过程分析的替代应用

除了 NMR 过程分析应用于不同原油调和之外，NMR 过程分析的其它一些应用非常有趣。

调和原油的兼容性

不同的原油调和，特别是涉及到非常规原油时，可能会出现沥青质沉降，这会引起管道和单元处理装置结垢。沥青质溶于极性芳烃，如甲苯，但不溶于极性烷轻溶剂。在线分析SARA含量(饱和轻，树脂，芳烃和沥青质）是一个潜在的工具，可以在线确定参加调和的不同原油间、或者原油与极性溶剂之间的定量比例。而不会导致沥青质沉降。

原油调和中的天然气凝析液

天然气凝析液（NGL）在气体装置和炼油厂制冷和蒸馏工艺中产生，并且被认为是在石油和天然气工业的副产物。为了利润，气体装置分离出天然气凝析液，并确保了管线天然气产品的质量。

启用在线 NMR 过程分析仪器为天然气凝析液和原油高效调和提供一个有效工具

NGL的价格相对较低，他们与从天然气中分离的其它不合格原料，被炼油厂的调和公司用于原油调和，以改善重油的品质。另一个用途是降低重油的粘度，改善它们在管道中的流动性。启用在线 NMR 过程分析仪器，为天然气凝析液和原油高效调和提供一个有效工具，这个工具能以最低的成本，提供调和所需要的物理属性。

结论

不同调和方案的存在是为了升级非常规原油为更高价值的合成原油。自动原油调和站集成了LP和NMR过程分析仪器，它即可以为提供调和服务的贸易商所用，也可以为炼油厂直接所用。成本、市场价格、可用和可以选择的技术，是用于升级非常规原油的规划配置中，将要去考虑的主要因素。

原油调和优化中，需要考虑两个主要技术：

任何时间、任何阶段，有在线过程分析仪器监测原油和调和油的质量品质。

动态仿真模型（调和仿真模型）通常用于确定所需要的调和油的组成。只有得到原油和调和油质量的实时分析数据去不断更新仿真程序，才能获得最好的调和优化。

使用 NMR 技术的过程分析仪器，能够测定黑暗和不透明介质的化学组成和物理属性。NMR波谱的好处，在于原油中分子的氢原子和原油组分的化学性质之间存在着线性相关关系，化学计量学把波谱测量转换为原油和调和油的特征物理性质。

这个技术在工艺中提供了调和原油的物理和化学性质实时数据和信息，能根据

提供的数据和信息在线调整和更改调和组分的量，直到取得所需要的物理性质为止。

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Advanced solutions for efficient crude blending

The use of nuclear magnetic resonance based process analysers supports the production of blends at lowest cost

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In the past, refineries were constructed to distill conventional light crude oils. Current economics, variations in the price of crude oils and shifting demand for distillates have forced refineries to reduce the cost of their distillation feedstock. Commonly, this is achieved by blending high-value light crude oils with heavy (unconventional) crude oils of inferior quality, or by buying ready-made blends. Low quality crudes include heavy crudes from known locations, as well as opportunity crudes that are brought on the market by traders worldwide. These crudes, of lower quality, can be purchased at low cost. Blending of these with costly crudes is inevitable to produce crude blends that bear optimal properties to be processed, and at minimum cost.

Refineries worldwide are constructed from an engineering point of view and from materials that enable the distillation of well-defined types of crude oils. These refineries were built based on the availability of certain types of crude oils in their neighbourhoods, the cost of certain crude oils on the market, and demand for predominantly light distillates for gasoline production.

Distillation of crude oil was mainly targeted to produce gasoline components, such as light and middle distillate. More recently and especially in the US and in Europe, demand for fuels has shifted from gasoline towards diesel fuels. This means that while in the past predominately light crudes were distilled, today refineries must be able to distil heavier crude oils to increase the amount of middle and heavier distillates. Refining margin for many refineries which were not able to adapt to the changing situations decreased. Technological limitations caused many refineries to buy expensive light crudes that do not produce specifically those distillates that are most needed in the market. For many refineries, the losses were too large. Many closed or changed their activities from distilling toward blending.

Nowadays, crude blending is performed either by blenders or by refineries themselves which buy various types of low cost crude oils. They upgrade their chemical and physical properties to produce a synthetic crude oil at lowest cost, which can be processed in refinery equipment and will yield high value distillate.

The additional cost of processing high TAN crude is within the range \$1.15–10.73/bbl, but the savings are \$43.54–62.7/bbl

Characteristics of crude oils

Quality properties determine the market value of each type of crude. The most important quality characteristics are the density, the total acid number (TAN) and the sulphur content. The API ranges from light crudes (high API, low density) to heavy crude oils (low API, high density). Sulphur is present in crude oils as hydrogen sulphide and as polysulphides. These sulphur containing molecules will partially decompose during distillation, while hydrogen sulphide evolves. The sulphur content and other acidic components in crude oil, such as naphthenic acids, are highly corrosive, and responsible for crude oil to be of a sour or sweet character. These characteristics mostly lead the price paid for different types of crude oils.

Refinery equipment

High TAN crude oils are characterised by fewer light components, high density and viscosity, low solidification point, high nitrogen content, high gel-asphalt content, high salts and high heavy metals contents and a low yield of light oil distillates. Oil separation in the desalter is more difficult than in conventional crudes. These properties also cause these crudes to give low quality products and they are very corrosive. Commonly, high TAN crude oils are called 'opportunity crude oils'. The price is about 80% that of conventional crude oil. The additional cost of processing high TAN crude is within the range \$1.15–10.73/bbl, but the savings compared to conventional crude processing are \$43.54–62.7/bbl. Utilising these crude oils in any way possible is therefore very attractive to refiners.[1]

In the past, most refineries were designed and constructed from materials according to the crude oil

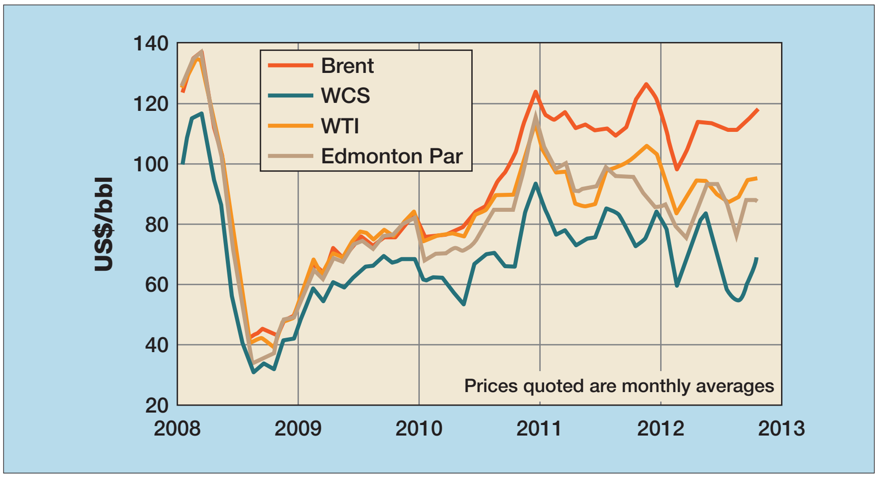


Figure 1 World oil price according to benchmarks

available and its ease of purchase. This limits the versatility of many refineries to purchase other crude oils of different qualities. Many of those refineries that are constructed to distil light and low sulphur crude oils are restricted as regards processing heavy fuels.

Critical differences in their physical and chemical properties make heavier crudes oils more difficult to distil than light crudes. Heavy crude oils are sour and more corrosive than light crudes. Higher viscosities, fouling tendencies and different flow streams make it more difficult to maintain stable crude charge rates, which are required for stable product yields, quality and reliability. Differences in boiling points between light and heavy crudes require different process temperature requirements such as pre-heating, different distillation temperatures, overheads and so on. Heavy fuels are rich in asphaltenes and metals and other contaminants which cause poorer desalting performance.

Product shifting

Demand for certain distillates and refinery products is shifting. It is expected that middle distillates will comprise some 45% of global demand per barrel by 2015, which is a rise of 10% compared to 2005. It can be expected that production of diesel gas oil in developing nations will increase by 10 million b/d from 2009 to 2030.[2]

The US is the largest consumer of crude oil. While US demand remains stable, today China is in second place with an annual 4% increase in demand for crude oil. New refineries, built nowadays, are already designed as such that they are not limited to a small range of crude oils.

The major operational cost of the refinery is contributed by the price of the crude oil, an estimated by 80-90% of cash flow. Reducing the cost of the crude feedstock, without changing the range and volumes of high valued distillates, increases the refining margin. Refinery profits are a direct outcome of the strategy applied by the refinery to purchase low cost crudes and to produce distillates with a high market value. To increase refining margin and remain competitive, refineries are obliged to minimise the cost of their crude feed, without affecting their capacity to produce high value distillates. As heavier crudes are more difficult to process, and with the increase of consumption of diesel oil as compared to gasoline, light sweet crude oils are marketed at a higher price than heavy crudes. Reducing the cost of the crude input, without changing the range and volumes of high valued distillates increases the refining margin.

Potential crude blenders

Two broad types of organisation deal with the business of crude blending, refineries and blend producers/trading companies. Crude blending is applied directly by refineries to prepare low-cost and compatible blends for internal consumption or for trading in the market. Efficient crude blending opens opportunities for oil blenders, oil trading companies and terminals to bring low cost blends onto the market. These blends can be sold to refineries with a high market value and quality.

Crude mixing can be applied throughout the entire supply chain of crude oil, from its well enabling transportation, through terminal blending to the refineries. The final crude supply to the distillation unit may be a combination of these activities.

The strategy of crude oil blending includes several parameters. Each of them contributes to the overall final cost of crude oil entering the crude distillation unit as well as the refining margin:

- The engineering limitations of crude distillation units to refine any type of crude oil
- Cost differences of crude oils according to their location of origin, and their chemical and physical properties. An increased ability to process unconventional crudes leads to improved refinery margin
- Product shifting in the market from gasoline towards diesel fuels. Increased demand for diesel fuels in the European market caused refineries to increase diesel yield over naphtha yield
- High viscosity, especially in heavier crude oils, affects the flow properties of crude during transportation. Blending these types of crude oils with diluents or conventional crudes may be required to reduce viscosity and to improve flow properties.

Crude oil economics

Previously, refineries distilled crude oil from single locations, but nowadays refinery profits are a direct result of the ability to create blends that include lesser quantities of high value crude oils and higher quantities of unconventional crudes, such as heavy and extra heavy crudes, sour crudes and bitumen extracted from oil sands. However, these blends should still have those physical and chemical properties that are required to enable smooth and continuous operation of the distillation unit at the lowest possible cost.

Basically, crude oils can be divided into four major groups:

- Light low sulphur (API 30-40°, S ≤0.5% mass)
- Light, moderate sulphur (API 30-40°, S=0.5-1.5% mass)
- Heavy, high sulphur (API 1-30°, S 1.5-3.1% mass)
- Extra heavy high sulphur (API = 15°, S ≥3% mass).

The ratio of a component in a blend is actually limited by the physical properties required for production of the highest valued distillates to the largest extent, and by the construction of equipment to process the blend.

Current values based on the benchmark of light Brent crudes and the somewhat heavier WTI crudes show differences in price of around $10/bbl a barrel (see **Figure 1**).[4]

Opportunity crudes are of course much cheaper. Various crude oils, such as some Venezuelan and Canadian crudes, are very heavy and are attractive for bitumen production. Their processing is limited by their very low API gravity. To produce other distillates from these crude oils, they must be upgraded by dilution with light crudes or kerosene.

The high viscosity of many of these heavy crudes is another drawback. Blending with light crude oils, kerosene or other diluents is also required to give them flow properties that enable their transport through pipelines without heating.

It is the aim of each refinery to maximise the consumption of opportunity crudes.

Heavy oils are hydrogen deficient and have high levels of contaminants such as sulphur, nitrogen, organic acids, vanadium, nickel, silica and asphaltenes. The method for upgrading heavy oils at relatively low cost is to dilute them with hydrogen rich, higher quality light crude oils or by using hydrogen rich diluents to increase the H/C ratio.

Blending processes

Crude oil blending can be performed by two technologies.

In-tank blending (batch blending)

Specific volumes of different kinds of crude oils stored in separate tanks are loaded into a blending tank where they are mixed until a homogenous composition is achieved. The tanks are mechanically stirred. Samples must be withdrawn to determine whether the blend is homogeneous and whether it conforms to its predetermined specification. In the event of discrepancy, correction of the blend must be conducted. The entire procedure of in-tank blending is very time consuming and expensive.

In-line blending

In contrast to tank blending, in-line blending is performed by simultaneously transferring different crude oils through an on-line static mixing device to the final blend tank. The predetermined flow ratio between the different crudes will provide a blend of the required quality. In-line blending enables on-line correction of the quality of the blend, by changing the ratio between feeds. The blend is produced instantaneously and no stirred 'blending tanks' are required.

To operate the blending process efficiently and without error, on-line process analysers are required to instantaneously measure the blend downstream and to feed the blending operators with the required quality details of the blend in production. This enables real-time and on-line correction during the blending process, providing the blend of predetermined properties. This reduces corrective re-blending of an entire tank, as well as unnecessary giveaways.

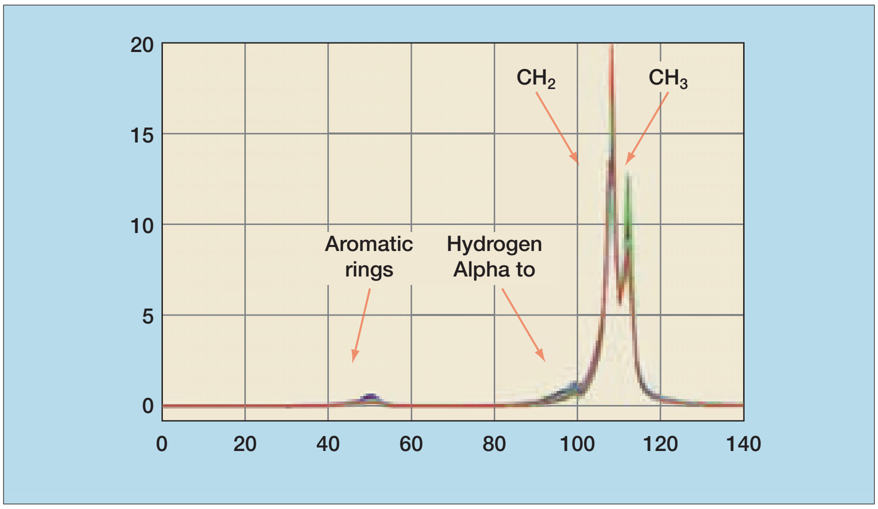


Figure 2 Typical NMR spectra of crude oils

Determination of blending recipes

Simulation software, such as linear programming (LP) modelling, is widely used to predict the ratio between individual components to prepare a blend. Based on the composition data of crudes used, and using the proper algorithm, this software is commonly applied to calculate and predict the physical properties of blends.

The software calculates the ratio of different crudes, resulting in a crude blend with the appropriate properties, leading to the desired distillates at optimal yields. Incorporation of a large database which covers a broad range of crude oils is required to predict accurately a blend of predetermined physical properties and with the potential to maximise production of high-value distillates. Adequate blending simulation models should include not only the chemistry of crude oil distillation but also its economics. It must be able to calculate the composition of different crudes to provide the best economic blend at the lowest cost. Such blends contain maximised volumes of those crude oils of lowest cost, but still bear the most attractive refining properties. This strategy will minimise variable costs and maximise profit.[5]

LP is based on the assay of different crudes oils to be blended. Any changes in the assay will affect the LP's predicted blend.

Fundamentally, effective crude blending simulation software should include the following features:[6]

- Calculation of the blend components and their ratios
- Ratio limits
- Predicted fraction temperatures
- Constraints in the properties of the blend
- Properties of the fractions
- Constraint limits.

Next to the chemico–physical properties of the blend, the software should also focus on the potential profit derived from the blend. This requires software also to relate to:

- Cost of various crude oils and crude oil blends
- Prices of final distillates and other refinery products.
- Volumes of final distillates required by the market

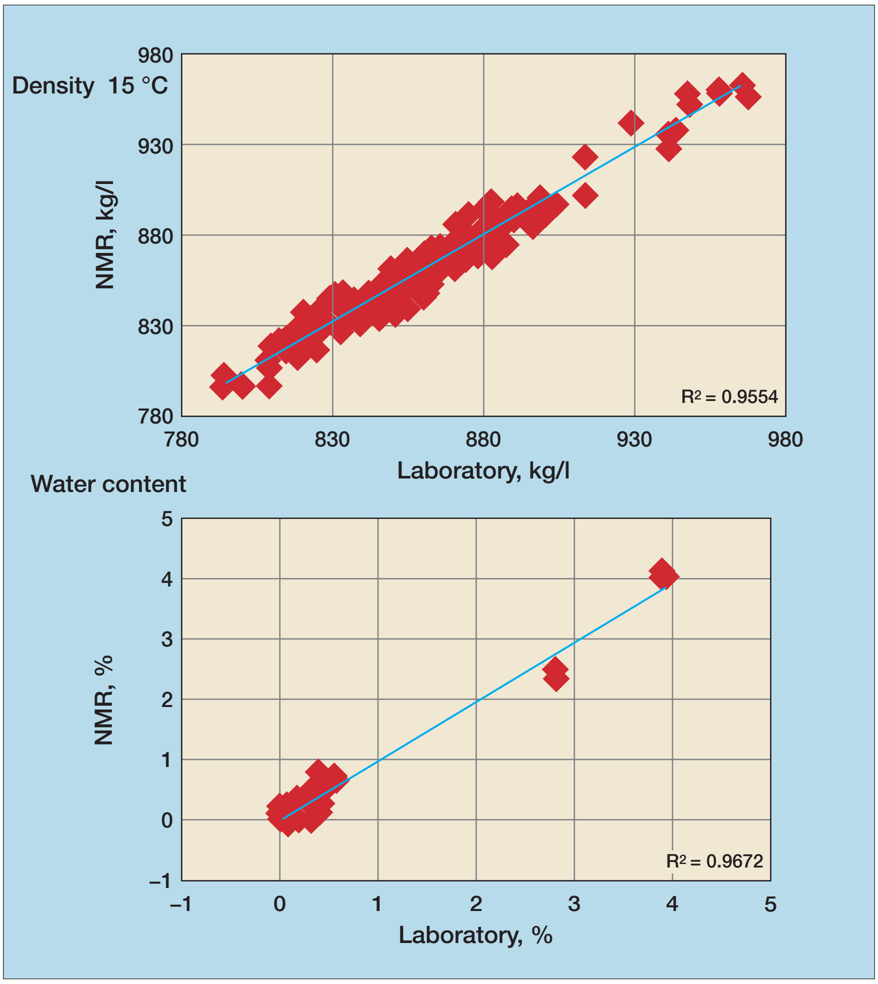


Figure 3 Correlation between NMR predicted results and laboratory measurements

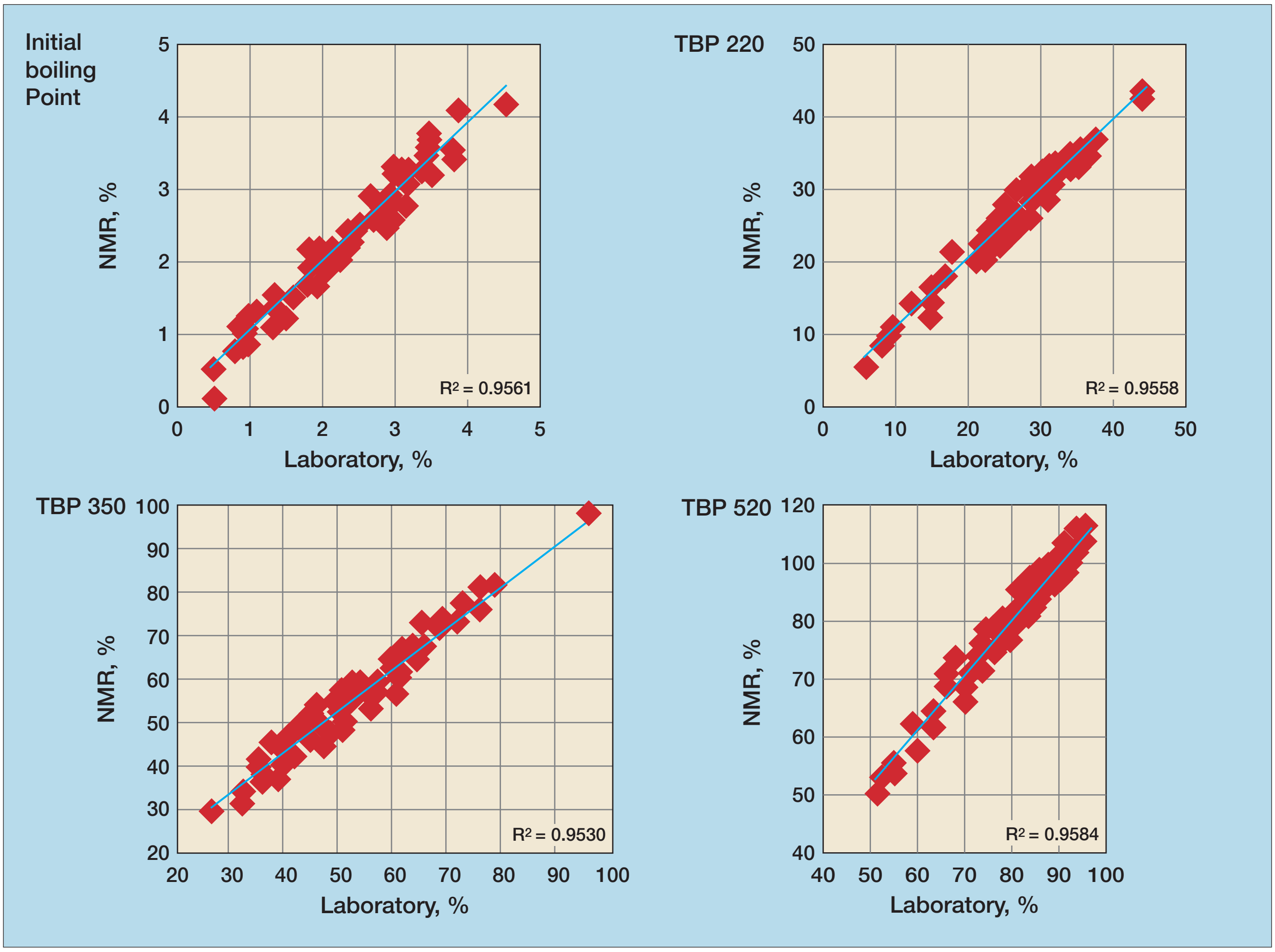


Figure 4 Correlation between NMR predicted boiling points and laboratory measured boiling points

Time consuming and costly laboratory analyses are required to verify the 'real' physical properties of the blend. Re-blending is required if these properties are not achieved.

Efficient blending requires on-line monitoring of the blend properties throughout its entire production. Chemical compositions differ from crude to crude. Notwithstanding whether the crude oil is pure, or a blend of crude oils, on-line corrections are continuously conducted to maintain stable product quality. This requires real time collection and validation of physical properties from the blend throughout its entire production process. Among all of the analysers available in the market, nuclear magnetic resonance (NMR) process analysers are the most suitable for that purpose.

The first NMR process analysers were launched in the late 1990s. In NMR, hydrogen nuclei in a magnetic field absorb and re-emit electromagnetic (EM) energy at a specific resonance frequency. The basics of NMR process analysers are the alignment of nuclei in a magnetic field. An external radio frequency (RF) pulse is applied; this distorts the alignment of the nuclei in the magnetic field. The resonance frequency depends mainly on the strength of the magnetic field. When the RF pulse ends, the protons relax and align back to their initial equilibrium position, which generates a decay signal, the free induction decay signal (FID).

Crude oil is a mixture of organic chemical compounds, mainly carbon and hydrogen-based molecules. Neighbouring atoms, such as carbon, oxygen and sulphur, and neighbouring chemical bonds, influence the strength of energy absorption and emission by hydrogen nuclei in a magnetic field. Accordingly, the signal of each hydrogen atom shifts differently in the NMR spectrum. These well-defined chemical shifts represent the chemical structure of molecular species. Linear correlation between the intensity of the signal and the hydrogen concentration makes it possible to quantify the different hydrogen nuclei.

Physical properties in crude oils and in distillates correlate with their chemical compositions. This allows chemometric methods to correlate between the measured spectral data and the physico–chemical properties of crude oil or other distillates. In contrast to other chemometric-based spectral technologies, such as Raman and NIR spectrometry, which are based on fingerprints, due to its molecular specificity and its linear quantitative correlation NMR technology requires far fewer reference samples to establish a chemometric model.

NMR-based on-line spectrometers are not limited to transparent fluids, but can be applied to transparent and opaque liquids alike. Crude oils contain water heteroatom molecules, which are easily distinguished by NMR spectrometry.

NMR on-line spectrometry with appropriate chemometrics has the ability to determine the following properties in crude oil:

- Specific gravity
- True boiling point yield
- Aromatic content, %
- Olefin content, %
- Pour point
- Water, %
- Sulphur, %.

Following these parameters is most important during crude blending. Their on-line measurement makes it possible to blend synthetic crude to deliver predefined properties, either from a physico-chemical point of view or from an economic point of view.

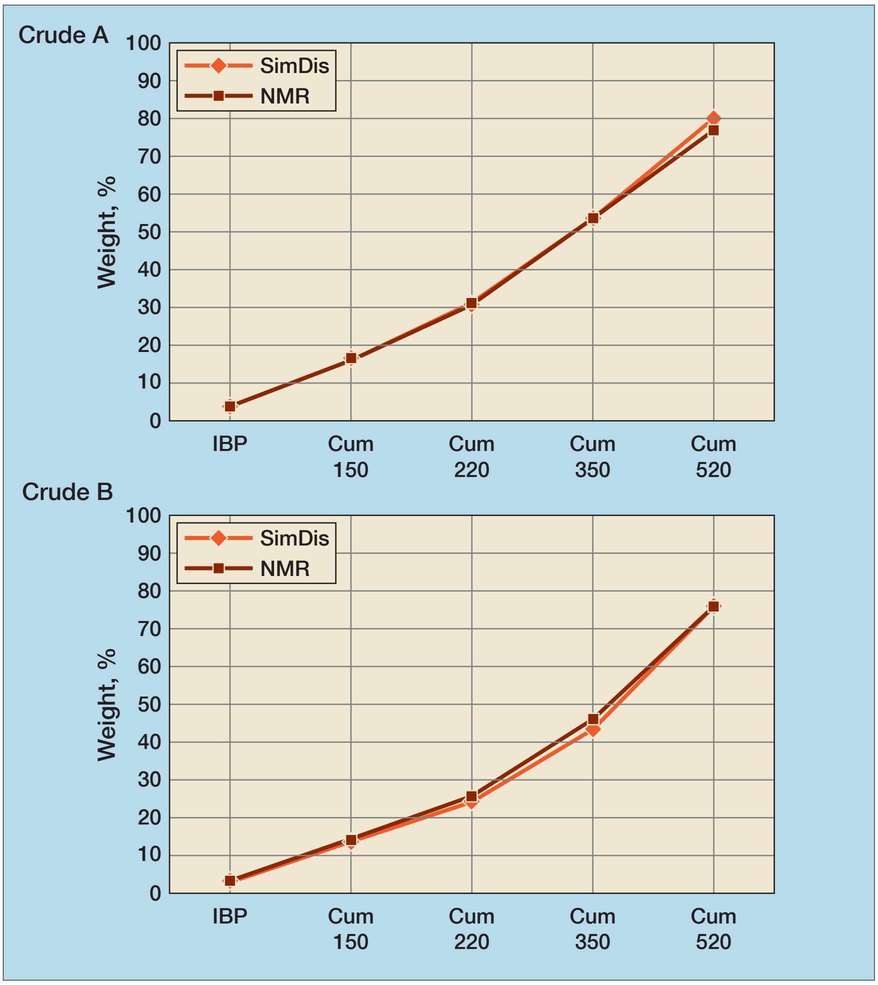
On-line monitoring of the blending process prevents the production of blends that do not comply with the requirements of the refinery. Blending errors and giveaways can be prevented which can lead to annual savings of millions of dollars.

Precision of NMR process analytics

High accuracy in the correlation between a NMR process analyser's results and laboratory results characterises the new generation of NMR process analysers. NMR magnets are sensitive to temperature differences. Earlier generations of NMR process analysers were especially sensitive to temperature differences due to the accumulation of heat produced by their electronics and heat-conducting measuring probes. In the new generation of NMR process analysers, the overall design excludes any accumulation of heat in the magnet or in its surroundings by uncontrollable fluctuations in temperature. This increased analysers' stability to heat fluctuation from ±2°C to ±10°C. This means that any heating of crude oil required prior to blending, or after the desalter, is possible without affecting the analytical results, as long as a temperature deviation of ±10°C is maintained.

Figures 3 to 5 show the correlation between an NMR analyser's predicted results and laboratory analyses of different crude oils.

The figures demonstrate the high accuracy in correlation between NMR predicted results and laboratory measurements. Partially these measurements relate to chemical matter such as water and sulphur, and partially to physical properties such as the distillation curve, and an excellent overlap between simulated distillation and NMR analytical results. Taking into account the time



Figures 5 Overlapping NMR and simulated distillation curves

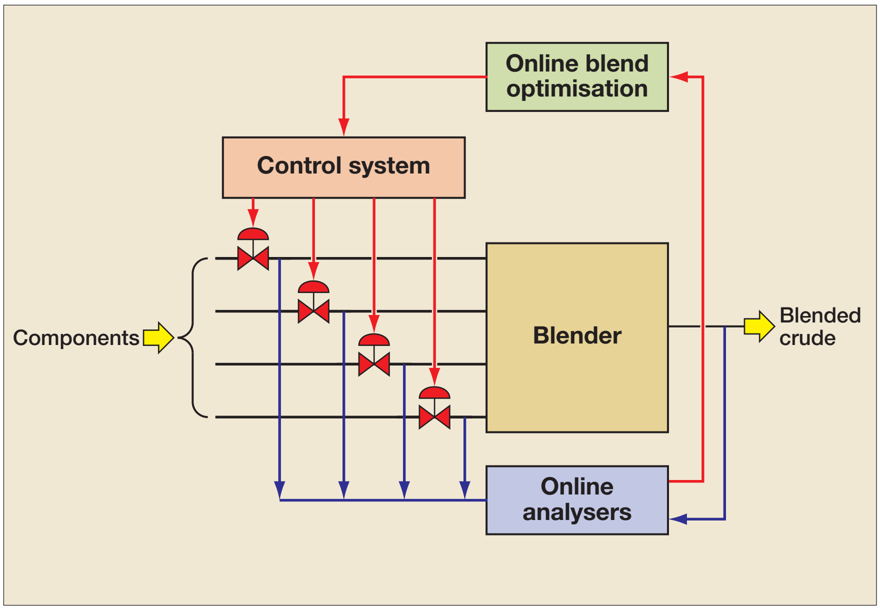


Figure 6 Set-up of a crude blending station with incorporated NMR process analyser, simulation modelling and blending control. (Components can be high and low quality crude oils, diluents and/or gasses (NLG)

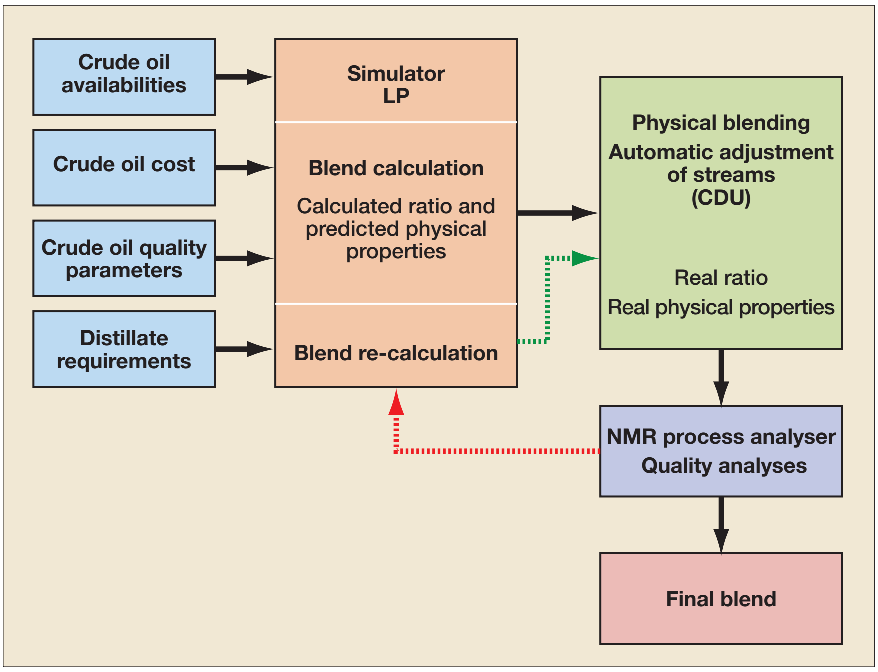


Figure 7 Dynamic process of mixing, continuous blend analyses, simulation model adjustment and process control

required for laboratory analyses, the cost to perform crude oil assays, or purchase and maintenance costs justifies the use of NMR process analysers in crude blending processes, especially in cases of in-line blending. NMR makes it possible to monitor precisely the quality of the blend in production and, if required, to change the ratio between different crude oil feeds to establish and maintain the quality of the final blend.

Optimised crude oil blending station

A crude blending station consists of a blending skid to receive liquid or gas streams, optimisation software and analytical equipment. Analytical equipment should be able to provide online measured data of component and product streams involved in a blending operation. This data is transferred to optimisation software whose target is to support production of a blended product with minimum product cost, minimal quality giveaway, and minimal deviation from individual raw material properties. To achieve this objective, the optimisation system continuously receives quality feedback of the finished product using on-line analysers.

Using the inputs from on-line analysers, the optimisation system performs either feed-forward or feedback control of raw materials based on the quality of product samples obtained from the blend header.

Both LP simulation and NMR process analysis can operate 'standalone'. However, for best optimisation of the crude blending process, it is essential to integrate the two technologies.

Implementation of on-line NMR process analysers provides an effective tool for efficient blending of NGLs and crude oil

Efficient blending optimisation is a dynamic process involving mixing, continuous blend analysis, simulation model adjustment and process control. All of these elements should be taken into account (see **Figure 7**). Any missing link in this chain of operations will impact the efficiency of the entire process and reduce its revenue.

Alternative applications of on-line NMR process analytic

Other uses of NMR on-line process analytics are of interest, in addition to the application of NMR process analysers for blending different crude oils.

Crude oil compatibility during blending

Blending different crudes, especially when unconventional crudes are involved, may cause precipitation of asphaltenes, which causes fouling in the pipes and process units. Asphaltenes are soluble in polar aromatics, such as toluene, but insoluble in paraffinic nonpolar solvents. On-line analyses of the SARA content (saturates, resins, aromatics and asphaltenes) can be a potential tool for on-line determination of quantitative ratio between different crudes to be blended, or between crude oils and polar solvents, without causing asphaltenes to precipitate.

Natural gas liquids in crude oil blending

Natural gas liquids (NGL) are produced by refrigeration and distillation processes in gas plants and refineries and are considered byproducts in the oil and gas industry. Gas plants extract NGLs for profit and/or to ensure production of pipeline quality natural gas.

NGL prices are relatively low. They and other off-spec materials from natural gas production are used by refineries and blending companies to upgrade heavy crude oils. Another application is lowering the viscosity of heavy crudes to make them flow more easily through pipelines. Implementation of on-line NMR process analysers provides an effective tool for efficient blending of NGLs and crude oil to deliver the required physical properties at lowest cost.

Conclusions

Different blending options exist to upgrade unconventional crude oil into synthetic crudes of higher values. An automatic crude blending station integrates LP with on-line NMR process analytics. It can be used either by traders who offer blending services, or directly by refiners. Cost, market value, availability and choice of technology are the main factors to be considered in planning a configuration to be used for upgrading unconventional crude oil.

Two principal technologies are required for optimised crude blending:

- On-line process analytics monitors crude oil and blend quality at any time and at any stage
- Dynamic simulation modelling (blending simulation models) are commonly used to determine the required blend composition. Highest blending optimisation can be achieved only by updating the simulation program with real time analytical data for crude oil and blend quality.

NMR-based process analysers can be used to determine chemical composition and physical properties in dark and opaque streams. The benefit of NMR spectrometry lies in its linear correlation between the hydrogen atoms of the molecules present in crude oil and the chemical nature of its components. Chemometrics transforms spectrometric measurements into the characteristic physical properties of crude oils and blends.

This technology provides real time data and information about the physical and chemical properties of the blend in process. On-line adjustments and changes between blend components can be performed accordingly until the required physical properties are achieved.

Thanks to Aspect imaging for their cooperation in NMR analysing crude oils.

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